

REMARKS

The word 'composite' has been added to claim 1 as suggested by the Examiner. Applicants have also amended claims 1 and 26 to provide that the composite dye particles are associated with a co-stabilizer which imparts colloidal stability to the particle; and that the dye is present during the polymerization of the polymer. These amendments will be discussed in detail in the following remarks.

Claims 1, 2, 4, 9-10, and 13 are rejected under 35 U.S.C. 102(b) as being anticipated by JP 041858672. Applicants respectfully traverse this rejection. Applicants have obtained a translation of the '672 reference and have submitted it with this response. The inks described in the '672 reference contain colored resin particles made by dye loading a preformed polymer. In contrast, the composite dye particles of the current invention are made by polymerizing the ethylenically unsaturated monomers in the presence of the dye. This is made clear by the process described at page 4, line 28 of the specification. The difference between starting with monomers and pre-loaded polymers is that the loaded polymers have poor colloidal stability due to the diffusion of dye into the polymers. It is difficult to describe what the structural difference is, but indirect evidence indicates that the particles have different ink stability. Additionally, with the process of the current invention more dye is associated with the polymer because the dye is encapsulated from the start by the formation of the polymer, rather than depending on diffusion of dye into the polymer. Claim 1 has been amended to require that the dye be present during the polymerization of the polymer.

Additionally, in the current invention the co-stabilizer is associated with the composite dye particle because it is present during the formation of the particle rather than being used to disperse the particle after formation. Also in the current invention both stabilizers (i.e. surfactants) and co-stabilizers are associated with the particles. There is no co-stabilizer present in the '672 reference. The additives discussed on page 8 of the reference are merely additional surfactants,

they are not co-stabilizers. In light of these differences the '672 reference cannot anticipate the current invention.

Claims 1-6, 9-16, and 19-25 are rejected under 35 U.S.C. 102(b) as being anticipated by Tsutsumi et al (U.S. 6,031,019) taken in view of the evidence of Howald (U.S. 6,153,667) and Helbrecht et al (U.S. 5,302,195). Applicants respectfully traverse this rejection. Again Tsutsumi describes polymer particles impregnated with dye wherein the dye is added after particle formation, see col. 12, line 61 and col. 3, line 65 to col. 4, line 20. Furthermore, Tsutsumi does not utilize a co-stabilizer that provides colloidal stability. The stabilizers described in Tsutsumi are light stabilizers, such as UV stabilizers, etc. This is a totally different concept. Applicants have amended claim 1 to provide that the co-stabilizer imparts colloidal stability to the particles. Support for this amendment is found at page 12, line 9 and at page 5, line 24. Also, please note Table 1 in which it is shown that composite dye particles prepared without a co-stabilizer agglomerate, while particles formed with a co-stabilizer do not. In light of these differences Tsutsumi cannot anticipate the current invention.

Claims 1, 2, 4-6, 9-10, and 13-23 are rejected under 35 U.S.C. 102(b) as being anticipated by Shimomura et al (U.S. 5,837,754). Applicant respectfully traverses this rejection. Again, Shimomura describes dye loaded polymers; see col. 5, line 7 which states that the colored particles are obtained by coloring a polyester resin. Additionally, in the current invention the co-stabilizer is associated with the composite dye particle because it is present during the formation of the particle. The polymeric stabilizers discussed in Shimomura are added after the preparation of the polymer dispersion and would not remain in association with the particles. Given these differences, Shimomura cannot anticipate the current invention.

Claims 1-2, 4, and 9-10 are rejected under 35 U.S.C. 102(b) as being anticipated by EP 1006161. Applicant respectfully traverses this rejection.. The '161 reference has no co-stabilizer. It only describes a traditional emulsion polymerization process and uses only stabilizers. Therefore, there is no co-stabilizer associated with the composite polymer particle. The other ingredients

discussed on page 18 of the reference appear to be added after the dispersion is formed and would therefore not be associated with the composite dye particle.

Claims 1-2, 4, 9-12, 14-16, 19, and 22-27 are rejected under 35 U.S.C. 102(e) as being anticipated by Ishizuka et al (U.S. 2001/0023267).

Applicant respectfully traverses this rejection. Again, Ishizuka describes dye loaded polymers; see paragraph 0247 to [0263] which provides that the coloring composition is obtained by mixing the oil soluble dye with the oil soluble polymer. Further, Ishizuka does not teach that both a stabilizer and a co-stabilizer should be utilized during dispersion. Therefore Ishizuka cannot anticipate the current invention.

Claim 7 is rejected under 35 U.S.C. 103(a) as being unpatentable over Tsutsumi et al (U.S. 6,031,019) or Shimomura et al (U.S. 5,837,754) either of which in view of Moore et al (U.S. 4,698,651). Applicant respectfully traverses this rejection. Shimomura and Tsutsumi have been discussed above. Since these references do not anticipate or make obvious the composite dye particles of the invention, and since Moore is not related to ink jet inks, the combination of the references cannot make the current invention unpatentable.

Claim 8 is rejected under 35 U.S.C. 103(a) as being unpatentable over Tsutsumi et al (U.S. 6,031,019) or Shimomura et al (U.S. 5,837,754) either of which in view of Evans et al (U.S. 6,001,161). Applicant respectfully traverses this rejection. Shimomura and Tsutsumi have been discussed above. Since these references do not anticipate or make obvious the composite dye particles of the invention, and since Evans does not discuss composite dye particles, the combination of the references cannot make the current invention unpatentable.

It is believed that these changes now make the claims clear and definite and, if there are any problems with these changes, Applicants' attorney would appreciate a telephone call.

In light of the above amendments and remarks, Applicants respectfully request that the claims as amended be allowed.

Respectfully submitted,

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(54) Title: INK-JET PRINTER INK AND A METHOD FOR FIXING* THE SAME

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* [In this context, "fixing" refers to an image-forming process.]

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[There are no amendments to this patent application.]

1. Title

Ink-Jet Printer Ink and a method for fixing the same

2. Claims

1. Ink-jet printer ink containing colored resin particles and an aqueous medium for dispersing the colored resin particles, characterized in that a water-soluble compound is dissolved in the aqueous medium to make the density difference between the aqueous medium and colored resin particle below 0.04.

2. Ink-jet printer ink containing colored resin particles and an aqueous medium for dispersing the colored resin particles, characterized in that the aqueous medium contains a water-soluble dispersion stabilizer for dispersing the colored resin particles in the aqueous medium.

3. A method for fixing ink-jet printer ink, consisting of a process of forming images by spraying an ink-jet printer ink containing colored resin particles having a glass transition temperature of 10-200°C and a medium capable of dispersing the colored resin particles through an ink-jet printer nozzle onto recording paper, and consisting of a process of heating the image by a heating means to melt the colored resin particles.

3. Detailed explanation of the invention

Industrial application field

The present invention concerns an ink-jet printer ink and its fixation, and more specifically concerns ink-jet printer ink and its fixation with no blotting on the recording paper.

Conventional technology and problems to be solved by the invention

Ink-jet recording has advantages of no need for processing such as development, etc., the use of plain paper as the recording medium, no noise in printing, capability of forming any characters, figures, etc., easy coloration, etc.

Conventionally, dye solutions have been used for ink-jet printer inks. When they are applied on recording paper, blotting of recorded dots occurs, causing the image to spread with reduced contrast, and recorded images lack water resistance.

Thus, for ink-jet printer inks using dyes, great efforts have been made to prevent blotting, e.g., (1) combining water, an organic solvent, and water-soluble dyes to reach a dye solubility in the solvent below 5 wt% and solvent content of 3-30% (Japanese Kokai Patent No. SHO 62[1987]-124166); (2) certain diether compounds are included in the ink (Japanese Kokai Patent No. SHO 62[1987]-32159); (3) use of inks containing hexose or its sugar alcohol-alkylene oxide adduct, pentose or its sugar alcohol-alkylene oxide adduct, glucose-alkylene oxide adduct, etc. (Japanese Kokai Patent No. SHO 62[1987]-15272, SHO 62[1987]-15273, SHO 62[1987]-15274); (4) use of water-soluble direct dyes and acid dyes freed of surface-active materials by adsorbent resins (Japanese Kokai Patent No. SHO 60[1985]-49070), etc.

Such inventions are effective for reducing the degree of blotting on the recording paper, but in principle, they are not able to completely prevent the spreading of inks around dots by capillary action of the fibers constituting the recording paper.

In Japanese Patent Application No. HEI 02[1990]-45686, for ink jet printer inks with the blotting of ink dots sprayed onto the recording paper, we proposed inks obtained by dispersing colored resin particles in aqueous media. With such inks, the aqueous media in the ink sprayed onto the recording paper penetrates into the recording paper, but the colored resin particles cannot pass through the voids between fibers of the recording paper, thus remaining on the recording paper, with no blotting.

For the prevention of blotting, the colored resin particles should have a certain size. However, as the colored resin particle size is increased, the dispersion stability of the colored resin particles during storage becomes poor. With a larger colored resin particle size, the dispersibility decreases due to Brownian motion. For example, when the colored resin particle density is heavier than the media, sedimentation occurs. Furthermore, large resin particles have a low degree of penetration into the recording paper, resulting in poor fixation of the colored resin particles onto the recording paper. Therefore, e.g., when touched with the hand, the recorded images may be smeared, causing poor readability.

The present invention is to overcome such drawbacks and it is an objective of the present invention to provide ink jet printer inks capable of forming high density, high contrast, high resolution images with excellent water resistance, without expansion of the ink dots initially formed on the recording paper, despite the penetration of aqueous media into the recording paper by capillary action. It is another objective of the present invention to provide ink jet printer inks with improved dispersion stability of colored resin particles during ink storage. It is still another

objective of the present invention to provide a method for the fixation of ink jet printer inks with improved fixation onto the recording paper.

Means for solving the problems

For achieving such objectives, the ink jet printer inks of the present invention consist of colored resin particles and an aqueous medium capable of dispersing the colored resin particles, with a water-soluble compound being added to the aqueous medium to make the density difference between the aqueous media and colored resin particles less than 0.05.

For achieving such objectives, the ink-jet printer ink of the present invention is also characterized by consisting of colored resin particles and an aqueous medium for dispersing the colored resin particles and containing a water-soluble dispersion stabilizer for dispersing the colored resin particles in the aqueous medium.

For achieving such objectives, the method for fixing ink-jet printer ink of the present invention consists of a process of forming images by spraying an ink-jet printer ink containing colored resin particles having a glass transition temperature of 10-200°C and a medium capable of dispersing the colored resin particles through an ink-jet printer nozzle onto recording paper, and involves a process of heating the image by a heating means to melt the colored resin particles.

Action

The ink jet printer inks of the present invention use colored resin particles as colorants in place of conventional water-soluble dyes, and the colored resin particles are dispersed in an aqueous medium. Thus, ink dots sprayed from the ink jet printer nozzle are not blotted. The penetration mechanism of such inks into recording paper is explained with Figure 1.

In step A of Figure 1, as ink is sprayed in the form of liquid drops (2) from ink jet nozzle (not shown) onto the recording paper (1), the liquid drops (2) collide with the recording paper (1) forming dots (5) as shown in step B. The liquid drop (2) contains colored resin particles (4) dispersed in a continuous phase of aqueous medium (3). As the dots (5) are formed, by the capillary action on the paper, the aqueous medium (3) is absorbed and penetrates, spreading in the horizontal and vertical directions of the paper but, as shown in step C, the colored resin particles (4) remain on the paper surface, maintaining the dot (5) form. Namely, by using the inks of the present invention, even when the aqueous medium penetrates and spreads onto the paper, blotting of the image does not occur. Yet, the image formed consists of colored resin particles accumulated on the paper surface, with a pigment effect, having the advantages of high density, high contrast, and excellent resolution. The image formed from the resin is resistant to water and is not redissolved even upon contact with water.

Particularly in the present invention, the dispersion stability of colored resin particles during storage can be improved by dissolving a water-soluble compound in the aqueous medium, resulting in a density difference between the aqueous medium and the colored resin particles that is below 0.04. Namely, when the colored resin particles have a much higher density than the aqueous medium, the sedimentation velocity of the colored resin particles obeys Stokes law, and sedimentation of colored resin particles occurs with the elapse of time, thus uniformly dispersed inks are not obtained. However, when the density difference between the aqueous media and colored resin particles is kept within a certain range, sedimentation of colored resin particles is prevented, and clogging by lumps formed by sedimented particles does not occur.

Furthermore, by including dispersion stabilizers in the inks, ink fixation can also be improved in addition to the ink dispersion stability improvement. This mechanism is explained with Figures 2(a) and (b). As shown in the figures, the dispersion stabilizer (7) is partially adsorbed on the surface of colored resin particles (4). As the ink is sprayed on the recording paper (1), since the dispersion stabilizer (7) has a very high affinity for the recording paper (1), the dispersion stabilizer (7) acts as a binder between the colored resin particles (4) and the recording paper (1), upon evaporation of the aqueous media after image formation, resulting in strong fixation of the colored resin particles (4) on the recording paper (1).

Furthermore, in the present invention, the ink fixation on the recording paper can be improved further by using colored resin particles with a glass transition temperature of 10-200°C and heating the ink sprayed onto the recording paper by a heating means for melting the colored resin particles, resulting in penetration of the molten colored resin particles between fibers and fusion of the molten colored resin particles together.

Preferred embodiments of the invention

The colored resin particles used in the present invention can be prepared, e.g., by the method given below.

As shown in process A of Figure 3, by emulsion polymerization or dispersion polymerization, an emulsion of spherical resin particles (4A) dispersed in an aqueous medium (3) is formed. The particle size of the resin particles (4A) should be controlled at the submicron level. Next, as shown in process B, a dye (6) such as a disperse dye, etc., is added into the emulsion to dye the resin particles (A). Next, as shown in process C, the dye is essentially completely exhausted to obtain colored resin particles (4). The resulting dispersion may be used as is or after being processed, as needed, for ink production for ink jet printer ink.

The resin particles may be polymer particles formed by emulsion polymerization or polymer particles formed by the post-emulsification (phase inversion method) of polymers, or

polymer particles obtained by dispersion polymerization, i.e., polymer particles obtained by polymerizing monomers in a solvent that dissolves the monomer but not the polymer formed.

Such resin particles should be at the micron or submicron level for dispersion stability and/or nozzle clogging prevention, preferably having a Coulter counter median diameter of 0.01-20 μm , more preferably 0.05-5 μm .

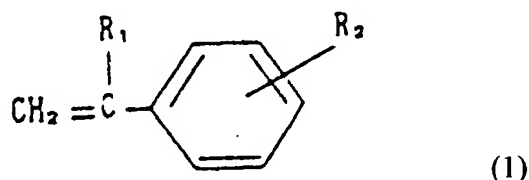
Other than the particle size control, the emulsion polymer and dispersion polymer particles can be prepared by any known method. For example, in emulsion polymerization, using an emulsifier such as a surfactant, etc., monomers are dispersed at the micron or submicron size level in an aqueous medium and polymerized in the presence of a radical polymerization initiator. In dispersion polymerization, monomers are polymerized in a solvent that dissolves the monomers but not the polymers formed. In the dispersion polymerization, for improved dispersibility of the colored resin particles, a dispersant or its combination with a dispersing aid can be used.

For post-emulsification (phase inversion process), for making emulsion polymers, a molten polymer or polymer solution is kneaded with an aqueous medium containing an emulsifier at high temperature and high pressure, if needed, to convert the polymer from the continuous phase to the disperse phase. This process is suitable for making emulsion polymers from polymers obtained by means other than radical polymerization.

The polymers may be olefin resins and olefin copolymers such as polyethylene, polypropylene, ethylene-propylene copolymer, ethylene-vinyl acetate copolymer, ionomers, etc.; aromatic hydrocarbon polymers such as polystyrene, styrene copolymers, etc.; acrylic polymers such as (meth)acrylic acid ester polymers, etc.; vinyl chloride polymers, polyamides, polyesters, polyvinyl acetal resins, epoxy resins, phenolic resins, etc.

In the present invention, for making resin particles with a fine uniform particle diameter, emulsion polymerization and dispersion polymerization are especially preferred; also, oil-soluble monomers, especially vinyl aromatic hydrocarbons and (meth)acrylic acid esters are preferred.

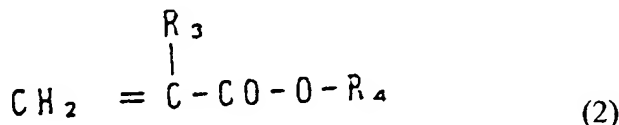
Vinyl aromatic monomers are vinyl aromatic hydrocarbons represented by the formula:



(In the formula, R_1 represents a hydrogen atom, lower alkyl group, or halogen atom; R_2 represents a hydrogen atom, lower alkyl group, halogen atom, alkoxy group, nitro group, or vinyl

group), e.g., one or two or more of styrene, α -methylstyrene, vinyltoluene, α -chlorostyrene, o-, m-, p-chlorostyrene, p-ethylstyrene, or divinylbenzene.

The (meth)acrylic acid ester monomers are acrylic monomers represented by the formula:



(In the formula, R_3 represents a hydrogen atom or lower alkyl group; R_4 represents a hydrogen atom, hydrocarbon group of up to 12 carbon atoms, hydroxyalkyl group, or vinyl ester group), e.g., methyl acrylate, ethyl acrylate, butyl acrylate, 2-ethylhexyl acrylate, cyclohexyl acrylate, phenyl acrylate, methyl methacrylate, hexyl methacrylate, 2-ethylhexyl methacrylate, β -hydroxyethyl acrylate, γ -hydroxypropyl acrylate, δ -hydroxybutyl acrylate, β -hydroxyethyl methacrylate, ethylene glycol dimethacrylate, etc.

Such oil-soluble monomers can be used alone, two or more of them can be used in combination, or they can be copolymerized with a small amount of water-soluble monomers, e.g., 1-30 wt%, especially 2-20 wt%, for resin particle modification, e.g., for improved dyeability or dispersion stability in water.

Such water-soluble monomers may contain at least one anionic group such as sulfonic acid, phosphoric acid, carboxylic acid, etc. Such an acid group may be in free acid form or in the form of alkali metal salts such as sodium salts, etc., ammonium salt, amine salt, etc. Suitable examples include styrenesulfonic acid, sodium styrenesulfonate, 2-acrylamido-2-methylpropanesulfonic acid, 2-phosphatoethyl methacrylate, 2-phosphatoethyl methacrylate, 3-chloro-2-phosphatoxypropyl methacrylate, acrylic acid, methacrylic acid, fumaric acid, crotonic acid, tetrahydrophthalic acid, itaconic acid, maleic acid, etc.

For emulsifiers, any known anionic or nonionic surfactants can be used in a concentration of 0-10 wt%, especially 0-5 wt%.

Excessive emulsifier in the system may cause ink jet nozzle clogging, thus it is preferred to use a minimum amount of emulsifiers for maintaining the dispersion stability of the resin particles. If surface-active materials are strongly adsorbed on the resin particles, emulsifiers may not be needed.

In general, the ratio of monomers to the aqueous medium is 1:99 to 50:50.

The polymerization initiators used for dispersion polymerization may be azo compounds such as azobisisobutyronitrile, etc.; peroxides such as cumene hydroperoxide, t-butyl hydroperoxide, dicumyl peroxide, and di-t-butyl peroxide, which are soluble in the oil-soluble monomers. The initiators that can be used in emulsion polymerization are potassium persulfate,

sodium persulfate, azobisisobutyramide hydrochloride, azobisisobutyramide nitrate, etc.

Ionizing radiation such as γ -rays, accelerated electron beam, UV rays, etc., may also be used in combination with various photosensitizers.

The amount of azo compounds, peroxides, etc., used is the so-called catalytic amount, in general 0.1-10 wt% in relation to the monomers used. The polymerization temperature and time are in the known range, in general 40-100°C and 1-50 h. The reaction system may be subjected to mild stirring for a uniform reaction, and the polymerization may be carried out in an inert gas such as nitrogen, etc., for the prevention of polymerization inhibition by oxygen.

In the dispersion polymerization, the organic solvents used are lower alcohols such as methanol, ethanol, isopropanol, etc.; ketones such as acetone, methyl ethyl ketone, methyl butyl ketone, etc.; ethers such as tetrahydrofuran, dioxane, etc.; esters such as ethyl acetate, etc.; amides such as dimethylformamide, etc., selected appropriately according to the type of monomers used. Such organic solvents may be used in combination with water for the control of resin particle precipitation.

For increasing the dispersion stability of resin particles, in addition to the surfactants described above, polymeric dispersion stabilizers may also be used, e.g., polyacrylic acid, polyacrylate salts, polymethacrylic acid, polymethacrylate salts, (meth)acrylic acid-(meth)acrylic acid ester copolymers, acrylic acid-vinyl ether copolymers, methacrylic acid-styrene copolymers, carboxymethylcellulose, polyethylene oxide, polyacrylamide, methylcellulose, ethylcellulose, polyvinyl alcohol, etc.

The dyes for dyeing the resin particles should be water-insoluble dyes for selective dyeing of the resin particles. Such water-insoluble dyes may be disperse dyes, water-insoluble metal-containing dyes, vat dyes, oil-soluble dyes, etc. Of these, for good dyeability, disperse dyes are desirable. Of course, under the conditions of no measurable presence of dissolved dyes in aqueous media, water-soluble dyes such as acid dyes, cationic dyes, and basic dyes can also be used. The amount of dyes used is in general 0.1-20 wt%, especially 1-10 wt%, in relation to the resin particles.

For dyeing the resin particles, the dyes described above are added to an aqueous dispersion of resin particles at a temperature at which the resin particles are not fused together. Such a treatment temperature may vary according to the type of polymers and dyes, while it should be below the resin-particle softening temperature + 40°C.

The colored resin particles thus obtained should have a glass transition temperature of 10-200°C, more preferably 30-70°C. In the present invention, resin particles having a glass transition temperature lower than the glass transition temperature of toner particles, according to the Carlson method, should be used. Therefore, resins having a relatively low glass transition temperature, which could not be used conventionally, can be used.

The ink jet printer inks of the present invention in general contain 1-50 wt%, especially 5-25 wt%, of colored resin particles in the aqueous medium.

The aqueous medium may be water or its mixture with water-soluble organic solvents, which may be organic solvents illustrated in the above dispersion polymerization process.

Furthermore, besides the aqueous media and colored resin particles, the inks of the present invention may also contain components desirable for dispersion, such as emulsifiers, dispersion stabilizers, dispersion aids, etc., originating from the dispersion preparation and compounding components desirable for inks. The dispersion stabilizers may be the water-soluble dispersion stabilizers described above, e.g., polyvinyl alcohol, sodium polyacrylate, starch, cellulose, polyethylene oxide, etc., which enhance fixation of the colored resin particles on the recording paper. When used for improving fixation, the amount of such water-soluble dispersion stabilizers used should be 10-200 wt% in relation to the resin particles.

The water-soluble compounds that are soluble in the aqueous medium, and which are used for reducing the density difference between the colored resin particles and the aqueous medium, may be inorganic compounds or organic compounds. Such water-soluble compounds should have a density above 1.00. Examples of inorganic compounds are given below.

Inorganic salts are especially preferred.

AgNO₃, AlCl₃, AlK(SO₄)₂, AlNH₄(SO₄)₂, Al(NO₃)₃, Al₂(SO₄)₃, As₂O₃, BaCl₂, Ba(NO₃)₂, BeCl₂, Be(NO₃)₂, BeSO₄, Br₂, CaBr₂, CaCl₂, CaI₂, Ca(NO₃)₂, Ca(OH)₂, CaSO₄, CdCl₂, Cd(NO₃)₂, CdSO₄, Ce₂(SO₄)₃, CoCl₂, Co(NO₃)₂, CoSO₄, CrCl₃, Cr(NO₃)₃, CrO₃, Cr₂(SO₄)₃, Cs₂SO₄, CuCl₂, Cu(NO₃)₂, CuSO₄, FeCl₂, FeCl₃, Fe(NO₃)₃, FeSO₄, Fe₂(SO₄)₃, H₃AsO₄, H₃BO₃, HBr, HCl, HClO₃, HClO₄, HF, HI, HIO₃, HIO₄, HNO₃, H₂O₂, H₃PO₄, H₂SO₃, H₂S₂O₃, H₂SeO₄, H₂SiF₆, H₂SO₄, H₂SO₄-HNO₃ mixed acid, HgCl₂, KBr, KBrO₃, KCl, KClO₃, KCrO₄, KCN, K₂CO₃, K₂CrO₄, K₂Cr₂O₇, KCr(SO₄)₂, KF, KFe(SO₄)₂, K₃Fe(CN)₆, K₄Fe(CN)₆, KHCO₃, KH₂PO₄, KHSO₄, KI, KIO₃, KMnO₄, K₂MoO₄, KSCN, KNO₂, KNO₃, KOH, K₂S, KSH, K₂SO₃, K₂SO₄, K₂SiO₃, K₂WO₄, La(NO₃)₂, LiBr, LiCl, LiI, LiNO₃, LiOH, Li₂SO₄, MgBr₂, MgCl₂, MgI₂, Mg(NO₃)₂, MgSO₄, MnCl₂, Mn(NO₃)₂, MnSO₄, NH₂OH, NH₂OH•HCl, NH₃, NH₄Br, (NH₄)₂CO₃, NH₄Cl, (NH₄)Cr(SO₄)₂, NH₄F, (NH₄)Fe(SO₄)₂, (NH₄)₂Fe(SO₄)₂, NH₄I, NH₄SCN, NH₄NO₃, (NH₄)₂SO₄, N₂H₄, N₂H₄•2HCl, Na₃AsO₄, NaBO₂, Na₂B₄O₇, NaBr, NaBrO₃, NaCl, NaClO₃, NaClO₄, Na₂CO₃, Na₂CO₃, Na₂CrO₄, Na₂Cr₂O₇, NaF, Na₂HAsO₄, NaH₂PO₄, Na₂HPO₄, NaHSO₄, NaI, Na₂MoO₄, NaNO₂, NaNO₃, NaOH, NaPO₃, Na₃PO₄, Na₄P₂O₇, Na₂S, NaSCN, Na₂S₂O₃, Na₂SO₃, Na₂SO₄, Na₂SnO₃, Na₂WO₄, NiCl₂, Ni(NO₃)₂, NiSO₄, Pb(NO₃)₂, PtCl₄, RbNO₃, RbOH, Rb₂SO₄, SnCl₂, SnCl₄, SrCl₂, Sr(NO₃)₂, ThCl₄, Th(NO₃)₄, Tl(NO₃)₂, Tl₂SO₄, UO₂(NO₃)₂, WO₃(H₂W₄O₁₃), ZnCl₂, Zn(NO₃)₂, ZnSO₄, water glass, and soda lime.

One, two, or more of the water-soluble compounds can be used. By dissolving such water-soluble compounds in the aqueous medium, the density of the aqueous medium can be

raised, resulting in a reduced difference in density between the colored resin particles and aqueous medium for improved dispersibility.

To enhance the wetting and rewetting of the colored resin particles, the inks of the present invention may also contain ethylene glycol, glycerin, or various polyhydroxy alcohols; various metal sequestering agents such as chelating agents for sequestering metal ions mixed into the inks; and various bactericides, anti-mildew agents, perfumes, UV ray absorbers, antioxidants, etc., for improved preservation of the inks and images.

Next, typical ink formulations (based on weight) are illustrated.

Colored resin particles	10-30	parts by weight
Surfactants	0.05-1	"
Water-soluble polymeric dispersant	0.01-20	"
Polyhydroxy alcohol	10-20	"
Chelating agent	0.5-1	"
Anti-mildew agent	0.1-0.5	"
Water-soluble compound	2-30	"
Water	50-200	"

Next, fixation of inks of the present invention is explained. As described above, the colored resin particles used in this method should have a glass transition temperature of 10-200°C, preferably 30-70°C.

The heating means used in the present invention may be any known means such as a hot roll, flash [-heating device], etc. By heating the ink sprayed onto the recording paper, the resin particles are melted for penetration of the resin particles between fibers of the recording paper and also fusion of resin particles together for improved fixation on the recording paper.

Effects of the invention

According to the present invention, by using colored resin particles as colorants for ink jet printer inks, blotting of ink dots is prevented, producing recorded images with a high density, high contrast, and high resolution, and the images have excellent water resistance and fixation. Furthermore, ink dispersion stability is enhanced, with the prevention of clogging. With improved image fixation, rubbing does not disturb the images.

Examples

Next, the present invention is explained in further detail with examples.

Application Example 1

In a 1-L separatory flask, 500 g of isopropyl alcohol, 170 g of styrene, and 5 g of 2,2'-azobisisobutyronitrile were stirred at 100 rpm and 70°C for 18 h to obtain resin particles with a volume-average particle diameter of 3 μm , then 15 g of an anthraquinone type of black disperse dye (BASF Palanil Black FD-BS) was dispersed into the flask and heated at 80°C for 5 h for dyeing, then filtered to obtain black resin particles.

10 g of the above black resin particles (density = about 1.05) and 1 g of tricalcium phosphate powder were dispersed in 90 g of an 8-wt% sodium chloride aqueous solution (density = about 1.05) to obtain an ink jet printer ink.

This ink was used for printing using an ink jet printer with a nozzle diameter of 70 μm , showing no blotting.

The ink was stored for 24 h, showing no visible sedimentation of particles.

Application Example 2

In a solution obtained by the complete dissolution of 1 g of high-molecular-weight polyvinyl alcohol (GL-03, degree of polymerization above 1500, partially saponified, product of Nippon Gosei Kagaku Kogyo Co.) and 20 g of low-molecular-weight polyvinyl alcohol (GH-17, degree of polymerization below 1000, partially saponified, product of Nippon Kagaku Kogyo Co.) in 90 g of water, 10 g of black resin particles were produced as in Application Example 1 to obtain an ink jet printer ink. This ink was used for printing using the printer used in Application Example 1, showing no blotting.

After being dried, the printed characters showed no smearing by rubbing with the hand.

Application Example 3

In a 1-L separatory flask, 400 g of isopropyl alcohol, 150 g of water, 130 g of styrene, 40 g of 2-ethylhexyl methacrylate, 1 g of divinylbenzene, and 5 g of 2,2'-azobisisobutyronitrile were stirred at 100 rpm and 70°C for 18 h to obtain resin particles with a volume-average particle diameter of 3 μm , then 15 g of azo black disperse dye (SPR Black #200, product of Mitsui Toatsu Senryo Co.) was dispersed into the flask and heated at 80°C for 5 h for dyeing, then filtered to obtain black resin particles. The resin particles had a Tg of 63°C as measured by differential scanning calorimetry (DSC).

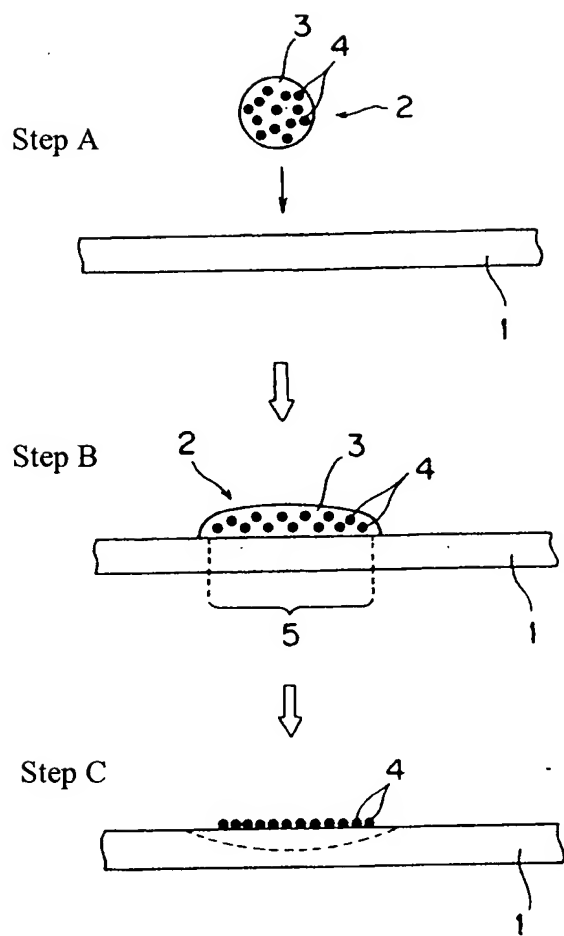
A black ink jet printer ink obtained from 10 g of the above black particles, 1 g of sodium dodecylbenzenesulfoante, and 90 g of water was used for printing using the same printer as in Application Example 1, showing no blotting.

The document printed using the above ink showed no disturbance in images under ordinary conditions, but when rubbed strongly with the fingers, the printed characters became

thinner. However, when this document was run through a thermal fixation machine at 180°C, the characters remained sharp even after strong rubbing.

4. Brief explanation of the figures

Figure 1 is a diagram explaining the functions of the ink jet printer ink of the present invention. Figures 2(a) and (b) are diagrams explaining the effects of fixation enhancement by a dispersion stabilizer. Figure 3 is a diagram explaining the manufacturing process of the ink jet printer ink of the present invention.



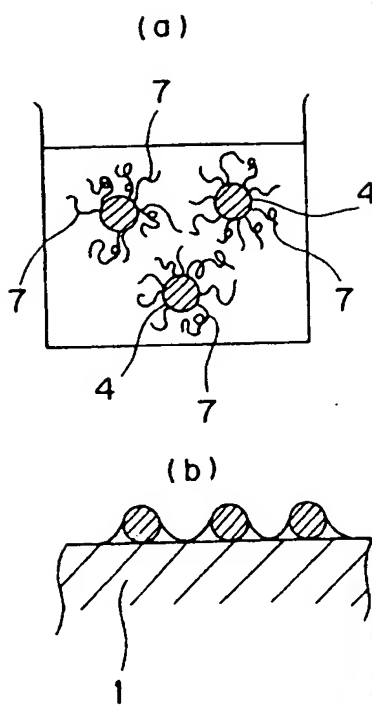


Figure 2

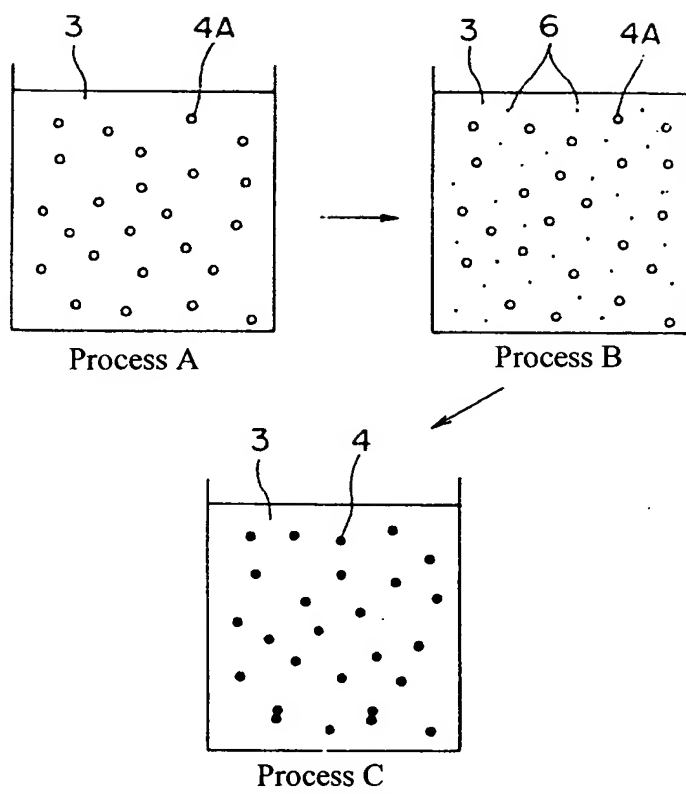


Figure 3

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INK-JET PRINTER INK AND A METHOD FOR FIXING THE SAME

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